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High efficiency energy transfer in Ce,Tb co-doped silica prepared by sol-gel method

H.A.A. Seed Ahmed a,b, O.M. Ntwaeaborwa a, R.E. Kroon a,*

Abstract

Amorphous Ce,Tb co-doped silica (SiO₂) was prepared using the sol-gel method with the aim of studying the energy transfer from Ce to Tb ions. It was initially found that adding Ce reduced the Tb emission intensity, implying that energy transfer did not occur. In fact, the Ce single doped sample exhibited very poor emission. Ultraviolet-visible diffuse reflectance measurements displayed the signature of non-luminescent Ce⁴⁺ rather than Ce³⁺ ions. We therefore annealed the samples in a reducing atmosphere of 4% hydrogen in argon gas at 1000 °C. The reduced Ce single doped samples exhibited bright luminescence and the diffuse reflectance measurements now showed the characteristic of Ce³⁺ ions. The reduced Ce,Tb co-doped samples excited at the Ce absorption wavelength gave characteristic Tb emission (with negligible Ce emission), indicating that very efficient energy transfer from Ce to Tb was achieved. For samples containing 1 mol% Tb, the maximum luminescence was found when co-doping with 0.5 mol% Ce. Using such co-doped silica samples exhibiting energy transfer, it is possible to obtain effective luminescence from the Tb³⁺ ions via excitation of Ce³⁺ ions at 325 nm, instead of exciting the Tb⁵⁺ ions directly which requires a shorter wavelength of about 227 nm.

Keywords: Amorphous materials Phosphors Sol-gel processes Luminescence Energy transfer

1. Introduction

Phosphors are widely applied in lighting, displays, lasers, scintillators, etc. Generally host materials should exhibit good optical, mechanical and thermal properties [1]. Microporous silica prepared by the sol-gel technique is considered to be an optically inert medium and its chemical and thermal stability increase its attractiveness as a host for luminescent ions [2]. Further advantages of the sol-gel process are that it can produce very pure glass at temperatures well below the melting point, and it allows incorporation of much higher concentration of dopants than the melt process [3,4]. Lanthanide group ions may be used as luminescent centres [5]. These ions have partially filled f-level electron shells, giving rise to various electron transitions in the UV, visible and IR regions of spectrum.

Energy transfer can play an important role in phosphor materials as it can be used to enhance the luminescence efficiency [6]. Ce³⁺ ions are an efficient sensitizer to Tb³⁺ ions and co-doping has been studied in a variety of hosts [7–13]. Tb ions are used as the activator because their bright green emission is suitable for many applications. Although Tb ions can be excited efficiently through their allowed 4f–5d transition, it can be advantageous to use Ce ions as a sensitizer because their allowed 4f–5d transition occurs at a longer (generally more accessible and convenient) wavelength. Tb and Ce can also be used to sensitize other lanthanides e.g. Tb may sensitize Sm in oxyfluoride aluminosilicate glasses to produce white light [14] and Ce may sensitize Yb in lithium–yttrium silicate glasses to produce near infrared light [15]. Ce ions can occur in a trivalent or a tetravalent state. Only the trivalent Ce³⁺ state with a single 4f electron is optically active, while the tetravalent Ce⁴⁺ ion is non-luminescent. Annealing in a reducing atmosphere can convert tetravalent Ce ions to the trivalent form, thus improving the Ce luminescence [16]. Ntwaeaborwa et al. [10] have reported some initial results on energy transfer from Ce to Tb in sol-gel silica. In this paper we report a much greater enhancement of the Tb luminescence excited via Ce at 325 nm in co-doped samples by annealing the samples in a reducing atmosphere, instead of air, in order to convert Ce from non-luminescent tetravalent ions to optically active trivalent ions.

2. Experimental details

Ce and Tb single doped, as well as Ce,Tb co-doped silica was produced using the sol-gel method by allowing tetraethylorthosilicate (TEOS) to react with water. Ethanol was used as a solvent, nitric acid was added to catalyze the reaction and Ce and/or Tb...
3. Results and discussion

Fig. 1 shows the XRD results of SiO$_2$:Ce 0.5 mol% annealed at 600 °C and 1000 °C. The sample annealed at 600 °C exhibited the well known characteristics broad peaks of amorphous silica [18,19], which narrowed slightly after annealing at 1000 °C, indicating a less disordered yet still amorphous sample. This is in contrast to the results of Nagpure et al. [20] who reported a low-quartz crystalline disordered yet still amorphous sample. This is in contrast to the XRD spectra for the samples due to the dopants, nor for those heated in a reducing atmosphere instead of air.

Fig. 2 shows the excitation and emission spectra of SiO$_2$:Tb 1 mol% annealed at 600 °C and 1000 °C. The optimum excitation wavelength of 227 nm is associated with the 4f–5d transition of well known characteristics broad peaks of amorphous silica [18,19], results of Nagpure et al. [20] who reported a low-quartz crystalline disordered yet still amorphous sample. This is in contrast to the results of Nagpure et al. [20] who reported a low-quartz crystalline disordered yet still amorphous sample. This is in contrast to the XRD spectra for the samples due to the dopants, nor for those heated in a reducing atmosphere instead of air.

The relatively high Tb concentration (1 mol%) allows cross relaxation which quenches emission from the 5D$_3$ level, whereas for a lower Tb concentration of 0.1 mol% in silica the 5D$_3$–7F$_5$ transitions are observed [22]. The Tb doped sample annealed at 1000 °C exhibited higher luminescence intensity compared to the sample annealed at 600 °C. In FTIR spectra (Fig. 3) the absorption near 3447 cm$^{-1}$ is attributed to the stretching vibration of hydroxyl ions (O–H), while the absorption near 1636 cm$^{-1}$ is attributed to water molecules. The three bands near 460, 798 and 1094 cm$^{-1}$ are characteristic of silica. The optimum excitation (1 mol%) allows cross relaxation which quenches emission from the 5D$_3$ level, whereas for a lower Tb concentration of 0.1 mol% in silica the 5D$_3$–7F$_5$ transitions are observed [22]. The Tb doped sample annealed at 1000 °C exhibited higher luminescence intensity compared to the sample annealed at 600 °C. In FTIR spectra (Fig. 3) the absorption near 3447 cm$^{-1}$ is attributed to the stretching vibration of hydroxyl ions (O–H), while the absorption near 1636 cm$^{-1}$ is attributed to water molecules. The three bands near 460, 798 and 1094 cm$^{-1}$ are attributed to the host silica Si–O–Si, O–Si–O and Si–O asymmetric stretching respectively [23]. Although the FTIR spectra of Fig. 3 are for Ce doped samples, the absorption bands are associated either with the host silica or the water and hydroxyl ions rather than the dopants which are present in low concentration and it is expected that similar results would be obtained for Tb doped samples. The FTIR results indicate that annealing at 600 °C could not effectively remove water and hydroxyl ions present in samples produced with the sol-gel process. The very high vibration frequency of the hydroxyl groups (3447 cm$^{-1}$) makes them very effective at quenching the Tb luminescence by allowing excited ions to decay non-radiatively through multiphonon relaxation. The Tb doped samples were annealed in flowing 4% hydrogen in argon gas for the same temperatures and time. Some samples were reduced in charcoal environment. Details of the preparation procedure have been published elsewhere [17]. X-ray diffraction (XRD) measurements were performed with a Bruker D8 diffractometer. A Bruker Tensor 27 was used to perform the Fourier Transform Infrared (FTIR) measurements from 4000 to 400 cm$^{-1}$. Diffuse reflectance spectra were recorded using a Lambda 950 UV–vis spectrophotometer equipped with a Cary Eclipse fluorescence spectrophotometer.
(less porous) silica that may account for part of the increased luminescence.

Fig. 4 shows the PL emission spectra of the Tb single doped and Ce,Tb co-doped samples annealed in air at 1000 °C using 325 nm as the excitation wavelength. Note that although 325 nm is not the optimum excitation wavelength of the Tb doped samples (see the excitation spectra in Fig. 2), nevertheless Tb emission is observed due to weak excitation within the f-levels of the Tb ions. Although the luminescence scale is much enlarged for Fig. 4 compared to Fig. 2, the spectrum of the Tb luminescence is similar. The 325 nm light was expected to excite the Ce ions in the co-doped samples and lead, through energy transfer to enhanced Tb emission. Unexpectedly, the PL emission intensity from the Tb ions was less in the Ce,Tb co-doped sample relative to the Tb single doped sample. This is in contrast to the result of Ntwaeaborwa et al. [10] where an enhancement in the Tb luminescence by a factor of about four times was reported. Sol-gel silica single doped with Ce and annealed in air did not show significant PL emission (Fig. 5). UV–vis diffuse reflectance measurements (Fig. 6) gave absorption which is characteristic of non-luminescent Ce⁴⁺ ions and is attributed to charge transfer from O²⁻ to Ce⁴⁺ [24]. The incorporation of Ce in the tetravalent state rather than the trivalent state means energy transfer will not occur in Ce,Tb co-doped samples, and in addition

Fig. 4. Emission spectra of SiO₂:Tb 1 mol% and of SiO₂:Ce,Tb 0.5,1 mol% annealed in air at 1000 °C.

Fig. 5. Excitation and emission spectra of SiO₂:Ce 0.5 mol% reduced with hydrogen at 1000 °C compared to the emission spectrum of SiO₂:Ce 1 mol% reduced with charcoal at 1000 °C and the emission spectrum of SiO₂:Ce 0.5 mol% annealed in air at 1000 °C.

the terbium emission may be reduced since a fraction of the incident light will be absorbed by the non-luminescent Ce⁴⁺ ions. However, in practice a mixture of Ce⁴⁺ and Ce³⁺ occurs [17] and the ratio could depend on the details of the sol-gel preparation method. It is suggested that the samples of Ntwaeaborwa et al. [10] may have contained a higher proportion of Ce³⁺ ions than those prepared in this study, which may have lead to the small enhancement of the Tb emission after co-doping with Ce.

To favour the formation of optically active Ce³⁺ ions, the Ce single doped samples were annealed in the presence of charcoal to create a reducing atmosphere. Such samples exhibited improved Ce luminescence (a broad blue emission band centred near 460 nm and attributed to 5d–4f transitions, with the excitation spectrum maximum near 325 nm), but much better results were obtained by heating in flowing 4% hydrogen in argon gas. Such reduced Ce single doped samples now exhibited intense PL emission (Fig. 5) and the UV–vis diffuse reflectance spectrum (Fig. 6) was characteristic of Ce³⁺ ions [26,27]. The conversion of Ce⁴⁺ to Ce³⁺ was also confirmed using x-ray photoelectron spectroscopy and the details have been published elsewhere [17].

Fig. 6. Diffuse reflectance of SiO₂:Ce 0.5 mol% annealed at 1000 °C in air and a reducing atmosphere (4% hydrogen in argon).

Heating in the reducing atmosphere instead of air did not have a significant effect on the FTIR results discussed earlier and a temperature of 1000 °C was still required for good luminescence results. Silica samples doped singly with Tb gave the same PL luminescence results irrespective of whether they were annealed in air or the reducing atmosphere, indicating that the Tb is incorporated in the host as Tb³⁺ ions. Fig. 7 shows the overlap region between the Tb excitation spectrum and the reduced Ce emission spectrum for singly doped silica samples, which is similar to that reported by Caldimol et al. for a zinc–sodium–aluminosilicate glass [12]. The Ce emission completely overlaps the ⁵D₄–⁷F₆ excitation band of Tb near 480 nm, while its energy edge also overlaps higher excitation bands of Tb, e.g. ⁵D₃–⁷F₆ near 380 nm, indicating that energy transfer may occur. Fig. 8 shows the PL spectrum of the Ce,Tb co-doped samples reduced at 1000 °C using 325 nm as the excitation wavelength. The emission spectrum for the single doped Tb sample from Fig. 4 is included for comparison, and now rather than the Tb emission of the co-doped sample being less than the singly doped sample, an enhancement due to energy transfer from the Ce ions of about 240 times is obtained. Similar enhancement of Tb emission by co-doping with Ce has been reported by Liu et al. [25], although in their case the Ce emission occurred at about 375 nm rather than the 460 nm reported here. Fasoli et al. [16] have reported from radioluminescence measurements that the dominant Ce emission is found near 2.7 eV (i.e. 460 nm), while emission near 3.1 eV (i.e. 400 nm) is found only in samples sintered in a reducing atmosphere...
which they suggest originates from Ce near the surface of amorphous Ce-rich clusters. From the excitation spectrum of Fig. 8 for the reduced co-doped sample measured for Tb emission at 545 nm one can see that the sample has excitation bands at 227 nm (Tb) as well as 325 nm (Ce). These excitation peaks are of similar height, and the Tb can be excited slightly more effectively via the Ce with energy transfer as when excited directly through the Tb f–d transition. The excitation spectrum of the co-doped sample reveals that the Ce emission intensity is only about 3% of the value obtained without Tb being present, meaning that with the assumption that there is no other mechanism to account for the reduction in Ce emission except energy transfer to Tb, the quantum efficiency for energy transfer from Ce to Tb is 97%.

To determine the optimum concentration of Ce which can give a high emission from Tb using 325 nm excitation, the concentration of Tb ions was kept constant at 1 mol% and the concentration of Ce ions was varied from 0 up to 4 mol%. Fig. 9 shows the relative intensity of Tb emission associated with the 5D4–7F5 transition near 544 nm as a function of Ce concentration using an excitation wavelength of 325 nm. The error bars represent a 2% error estimate, obtained by repeating the measurement of one sample 10 times in succession. We attribute this to the effective conversion of Ce3+ ions to Ce4+ ions in our samples through annealing in a reducing atmosphere.

4. Conclusion

From these results it is clear that the details of how Ce-doped silica is produced using the sol-gel method can affect how much Ce is incorporated in the trivalent or tetravalent charge state. It may be possible to obtain a small but effective concentration of Ce3+ even when annealing in air as demonstrated by Ntwaeaborwa et al. [10], or almost all the Ce may be incorporated as non-luminescent Ce4+ as in this study. However, for good Ce luminescence in single doped samples, and for enhanced Tb emission via energy transfer from Ce in co-doped samples, it is important to anneal the samples at a higher temperature (1000 °C) than 600 °C as widely reported for sol-gel silica samples and to use a reducing atmosphere instead of annealing in air. The Tb emission in co-doped Ce,Tb silica samples prepared in such a way can be excited as effectively, via absorption of Ce3+ ions at 325 nm together with energy transfer, as by direct excitation of the Tb f–d absorption band near 227 nm. For a Tb concentration of 1 mol%, the optimum concentration of Ce co-doping was found to be 0.5 mol%.

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